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Effects of sodium borohydride as a reductant on the synthesis conditions of Nano-scale Zero Valent Iron

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Abstract: Nano-scale Zero Valent Iron (NZVI) has appeared as one of the Nano-engineered materials for the environmental remediation. Chemical reduction reaction method extensively used to prepare the Nano iron. In this study; in order to optimize the reactivity, NZVI was prepared under different synthesis conditions by adjusting several variables such as concentration, delivery rate and liquid volume of sodium borohydride. The reactivity of NZVI was evaluated by reacting the iron with two environmental contaminants; nitrate and phosphorus. NZVI was synthesized with different ratios of $\text{NaBH}_4/\text{FeCl}_3$ and the reactivity of Nano iron increased with increasing the ratio of NaBH_4 . On the other hand, excessive amount of NaBH_4 resulted in decreasing the reactivity. The faster feeding rate of NaBH_4 resulted in increasing the reactivity toward the nitrate and phosphorus but increasing it largely led to deterioration of the reactivity. Impact of sodium borohydride liquid volume was studied and high reactivity was observed under high liquid volume. The results of this study show the optimization of NZVI production parameters could minimize the cost and maximize the reactivity.

Keywords: nano-scale zero valent iron; synthesis conditions; reductant delivery rate; optimization of NZVI production

1. Introduction

NZVI technology has emerged as one of the most important Nano engineered material for environmental remediation. Due to it is high efficiency, NZVI has been widely used to remove the environmental pollutants from water such as heavy metals, chlorinated compounds, etc. Moreover, NZVI can be reacted with different contaminants by the different mechanisms including: reduction, oxidation, adsorption, absorption, precipitation, and coprecipitation mechanism. Therefore, NZVI can be used to remove a wide variety of environmental pollutants. In addition, NZVI shows a successful strategy for treating groundwater by applying it in a permeable reactive barrier, which permitting groundwater to flow through it, then the groundwater is treated.

NZVI can be prepared by two different methods, first “Top down” method. The main idea of this method is the milling or break down of micro iron particles to become in Nano scale. On the other hand, NZVI can be prepared by “bottom up” method; under this method micro particles can be converted to Nano particles by applying the chemical reduction reaction such as reduction of ferric or ferrous iron with a strong reductant. Chemical reduction reaction is considered as the most popular method to fabricate Nano materials. The advantages of this chemical method are its simplicity and chemical homogeneity and also NZVI can be synthesized by this method without any special equipment. Besides that, NZVI particles prepared by this method display high reactivity compared with “Top down” method. [1].

Furthermore, it is possible to control the properties of NZVI such as particle size, shape, and surface area and also the chemical method exhibits low cost compared with Top down method. In contrast, it is difficult to control and enhance the properties of NZVI such as particle size and surface area by top down method [2].

Controlling of synthesis conditions is considered as one of the most effective methods to manipulate the properties of NZVI [3]. Accordingly, the reaction medium plays an important role to decrease the particle size and increase the surface area of NZVI particles. It was reported that the reactivity of NZVI depends on its size [4]. In addition, adjusting and improving the dispersibility of NZVI particles can occur in the reaction medium by where the stabilizer is added [5]. Few studies confirmed that synthesis conditions strongly affect the properties and reactivity of NZVI. It was reported that the reactivity of NZVI was improved under high precursor concentration and faster delivery rate [6]. In contrast, HAN et al. [7] reported that preparing NZVI at high Fe^{3+} concentration refer to dwindle the reactivity and he contributed that to formation oversize of NZVI particles. Sodium borohydride was studied as an important parameter on NZVI reactivity. Hwang et al. [8] discussed the impact of sodium borohydride and he found that the reactivity was improved with high sodium borohydride concentration. In contrast, Hocheol Song et al. [9] confirmed that the reactivity of NZVI was increased under low concentration of sodium borohydride and they attributed that to the low pH value. Based on that effect of synthesis variables have not been extensively studied so far.

The objective of this study is to optimize the parameters of synthesis conditions such as concentration, feeding rate, liquid volume of sodium borohydride, temperature, pH value and mixing speed to maximize the reactivity and minimize the cost of synthesis. Therefore, a wide range of these variables was investigated in order to obtain the optimal ratio for each variable. In addition, the characterization of NZVI such as particle size, surface area and pore size have been investigated characterizations on the reactivity of NZVI toward environmental pollutions.

Table 1. NZVI synthesis conditions.

| No. | [NaBH ₄] (M) | NaBH ₄ delivery rate (ml/min) | NaBH ₄ liquid volume (ml/L) | Parameter |
|-----|-----------------------------|--|--|------------------------------------|
| 1 | 0.22 | 20 | 60 | NaBH ₄ Conc. |
| 2 | 0.45 | 20 | 60 | |
| 3 | 0.56 | 20 | 60 | |
| 4 | 1.12 | 20 | 60 | |
| 5 | 2.25 | 20 | 60 | NaBH ₄ delivery rate |
| 6 | 1.12 | 2.5 | 60 | |
| 7 | 1.12 | 10 | 60 | |
| 8 | 1.12 | 20 | 60 | |
| 9 | 1.12 | 40 | 60 | NaBH ₄ liquid volume |
| 10 | 1.12 | 60 | 60 | |
| 11 | 1.12 | 20 | 10 | |
| 12 | 1.12 | 20 | 30 | |
| 13 | 1.12 | 20 | 60 | |
| 14 | 1.12 | 20 | 120 | |

2. Materials and methods

2.1. Chemicals.

Ferric chloride (FeCl₃) and sodium borohydride (NaBH₄) were used as inputs to interact to produce and fabricate NZVI. Sodium nitrate (NaNO₃) was used to prepare nitrate solution and potassium dihydrogen phosphate (KH₂PO₄) was used to prepare phosphorus solution. Ethanol was used for washing process.

2.2. Synthesis of NZVI

In this study, chemical reduction reaction method was used to fabricate NZVI using sodium borohydride as a strong reductant to reduce ferric chloride. Synthesis of NZVI was carried out in round bottom four neck flask. The stirrer was inserted in the middle neck and nitrogen gas was injected in one of the opens neck to avoid iron oxidation. The other two slots were used to add NaBH₄ to the reaction medium and also to allow the resulting gases to exit. Different experiments were conducted to prepare NZVI at different synthesis conditions as shown in table 1. The 1st – 5th experiment were carried out to detect the influence of NaBH₄ concentration on NZVI reactivity. In addition, the 5th -10th experiment were conducted to test the effect of NaBH₄ feeding rate on NZVI reactivity. On the same path 4th experiments were conducted to evaluate the effect of NaBH₄ liquid volume on NZVI reactivity. All the experiments were carried out at a constant temperature 25 C and constant mixing speed 250 rpm. The synthesis of NZVI was conducted according to this equation.



The reaction solution was left for 20 min as agent time and then the NZVI was filtered using vacuum filtration. The filtered particles were washed three times with ethanol solution.

2.3. Evaluation of NZVI reactivity.

Batch tests of nitrate reduction and phosphorus removal were carried out to detect the effect of synthesis condition on NZVI reactivity. The reactors were filled with 200 ml of phosphorus which contained 50 mg/L phosphorus and 200 ml of nitrate which contained 200 mg/L nitrate. Both of nitrate and phosphorus solutions were purged with nitrogen gas before adding 0.25 g of NZVI for each of them to avoid the oxidation process. The solutions were placed on the environmental shaker

for two hours and the samples were taken periodically and then the taken samples were filtered with 0.25 syringe. Finally, the samples were analyzed immediately using spectrophotometer device.

3. Results and discussion.

3.1. Effect of NaBH₄ concentration on NZVI reactivity

A series of Nano-scale Zero-valent Iron synthesis experiments were carried out with different concentration of NaBH₄. These experiment were conducted to detect the impact of NaBH₄ on the performance of NZVI toward two environmental contaminants, nitrate and phosphorus. Different amounts of NaBH₄ concentration (0.22, 0.45, 0.56, 1.12, 2.25 M) were dissolved in water in order to reduce constant amount of FeCl₃ (0.15 M) and also under constant conditions of other variables such as pH value, temperature, NaBH₄ feeding rate and mixing speed. The reactivity of NZVI was changed at different concentrations of NaBH₄ as shown in Fig.1. a and b. The removal efficiency of phosphorus and nitrate reduction were deteriorated significantly at low NaBH₄ concentration. On the other hand, synthesizing NZVI at high NaBH₄ concentration improved the phosphorus removal and nitrate reduction. However, increasing the NaBH₄ concentration to a large extent led to deteriorating the reactivity. Therefore, the optimum ratio of NaBH₄ to FeCl₃ (1: 3) M was investigated to achieve the best removal of phosphorus and nitrate reduction.

The reactivity of resultant iron depends on the reduction of FeCl₃ by NaBH₄, based on that, preparing the Nano iron at low NaBH₄ concentration means that there is no sufficient amount of sodium borohydride to reduce FeCl₃. Therefore, the reaction does not occur completely and thus leading to deteriorating the reactivity of NZVI. The high concentration of NaBH₄ led to decrease the reactivity due to increased pH value. Increase the pH value reduced the chance to dissolve non-reactive precipitated solids (Hocheol Song, 2005) [10]. And also during the addition of sodium borohydride not only the reaction between NaBH₄ and FeCl₃.6H₂O synthesized NZVI but also other products such as iron hydroxides could be formed and this effect negatively on the reactivity of Nano iron. Adding to that, different NaBH₄ concentration gave different particles size as well as different reactivity (Meral Turabik,2016) [11].

3.2. Effect of NaBH₄ liquid volume on NZVI reactivity

Several experiments were carried out to evaluate the impact of sodium borohydride liquid volume at a constant concentration of FeCl₃ on NZVI reactivity. Different liquid volumes of NaBH₄ (10, 30, 60, 120 ml) were used to test the effect of NaBH₄ liquid volume on NZVI reactivity. The finding from this study confirms that increase sodium borohydride liquid volume led to increase the reactivity of Nano iron toward phosphorus removal and nitrate reduction as shown in fig.2. (a) and (b). During synthesis process of Nano iron particles, preparing of Nano iron particles pass through important stages such as nucleation, development, growth and agglomeration stage. Stages of growth and development

a

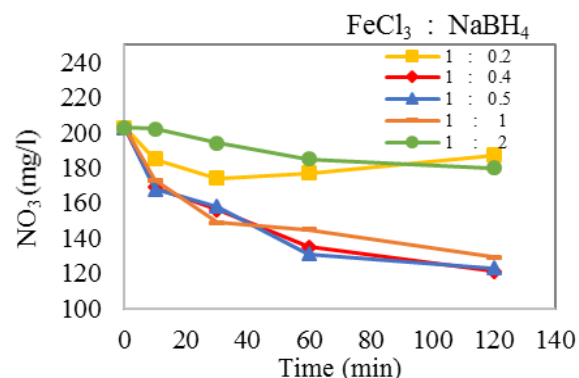
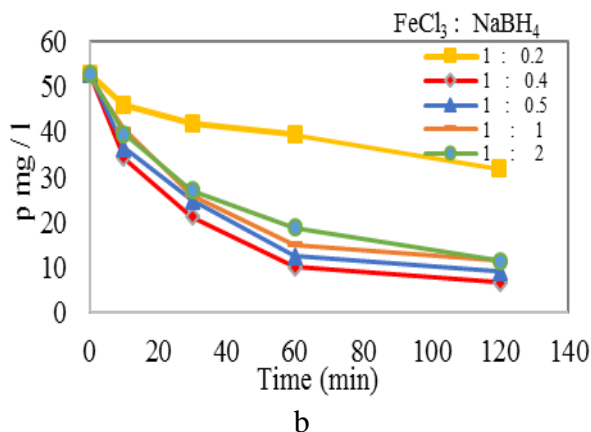


Fig.1. effect of different sodium borohydride concentration on NZVI reactivity (a) phosphorus removal (b) nitrate reduction

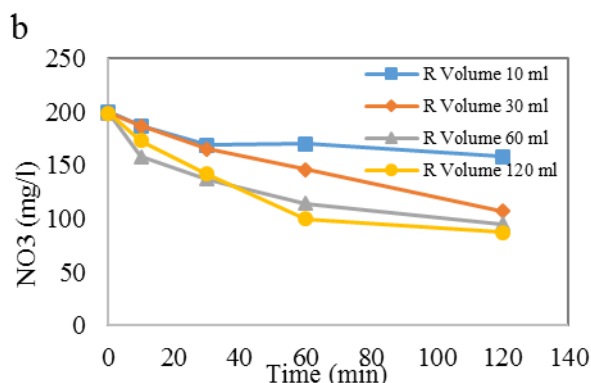
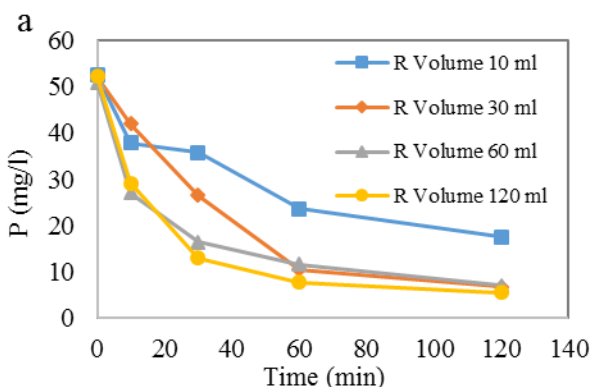


Fig.2. effect of different sodium borohydride liquid volume on NZVI reactivity (a) phosphorus removal (b) nitrate reduction.

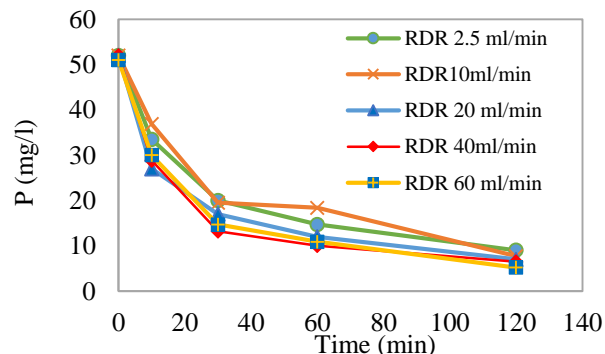
of Nano iron particles requires enough time during synthesis of Nano iron particles. The improvement of Nano iron reactivity at high sodium borohydride liquid volume due to increase the period of sodium

borohydride added. It is necessary to adjust the volume of NaBH₄ to control the reaction time and the properties of the - resultant iron such as particle size (Yu-Hoon Hwang, 2011) [12]. Overall, sodium borohydride liquid volume affected significantly on the characteristics and reactivity of NZVI

3.3. Effect of NaBH₄ delivery rate on NZVI reactivity

In this study, the effect of NaBH₄ delivery rate on NZVI reactivity was evaluated by phosphorus removal and nitrate reduction efficiency. NaBH₄ was added to FeCl₃ at different flow rate (2.5 ml (2 rpm), 20 ml (10 rpm), 40 ml (18 rpm), 60 ml (25 rpm)). Feeding rate showed a significant impact on the reactivity and properties of NZVI such as surface area, shape, and the size of NZVI particles. High surface area, and tiny particles were observed under high NaBH₄ delivery rate but core-shell structure (spherical particles) was observed under low delivery rate but scattered particles was observed under high delivery rate (Yu-Hoon Hwang 2011) [13]. Therefore, NaBH₄ delivery rate play an important role to control the properties and morphology of NZVI particles. Change of NZVI properties this leading to a different performance of NZVI toward nitrate reduction and phosphorus removal. The faster feeding rate of NaBH₄ to FeCl₃.6H₂O resulted in enhance the reactivity but excessive delivery rate led to deteriorate the reactivity as shown in fig .3. a and b. The improved reactivity at faster feeding rate of NaBH₄ contributed to decreasing pH value (Hocheol Song 2005) [14].

a



b

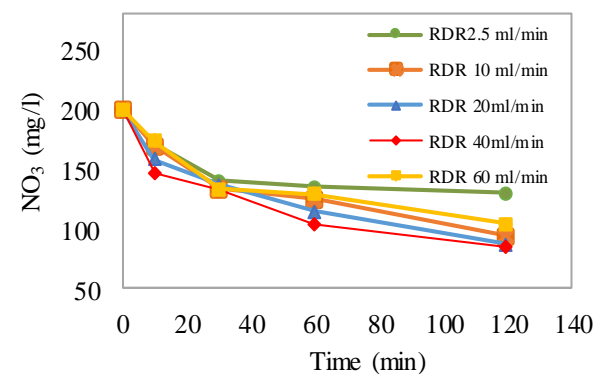


Fig.3. effect of different sodium borohydride delivery rate on NZVI reactivity (a) phosphorus removal (b) nitrate reduction.

4. Conclusions.

In this study, the effect of reaction condition such as concentration, liquid volume and feeding rate of sodium borohydride was evaluated. The Concentration of Sodium borohydride clearly affects the reactivity of NZVI. Increasing the mass ratio of ferric chloride to sodium borohydride from 1:0.2 to 1:0.4 led to increasing the reactivity. On the other hand, the increase of mass ratio more than 1:0.4 led to deteriorating the reactivity of NZVI. Therefore, 1:0.4 is considered the optimum mass ratio to preparing NZVI with investigating high reactivity. The pumping speed up to 40ml/min of sodium borohydride led to enhance the reactivity of NZVI. But excessive feeding rate led to dwindling the reactivity. Sodium borohydride liquid volume exhibited a significant impact on NZVI reactivity. The result from this research confirm that increase sodium borohydride liquid volume up to 120 ml/L showed enhancing in the reactivity of NZVI.

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